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# Solubilisation of Oils in Aqueous Solutions of a Random Cationic Copolymer

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## Abstract

*Hypothesis.* Reports of random copolymers capable of solubilising hydrophobic oils are rare. This is primarily because random copolymers are unlikely to self-assemble into suitable aggregates (or micelles) in water. A random copolymer with a "blocky" (or lumpy) microstructure may have potential to solubilise hydrophobic oils in water. This type of polymer would have advantages over block copolymers which are more laborious and costly to synthesise.

*Experiments.* The solubilising capacity of a blocky random copolymer, namely poly(methyl methacrylate-*co*-2-dimethylaminoethyl methacrylate) (PMMA-*co*-PDMAEMA) is assessed by UV-visible spectroscopy and compared with common reference surfactants. The relative solubilising performance of random copolymers (across a narrow range of DMAEMA mol % fraction) for aromatic and aliphatic oils was also studied. The morphology of the aggregates was monitored as a function of the solubilisation capacity by small-angle neutron scattering (SANS) and dynamic-light scattering (DLS).

*Findings.* Similarly to well-defined block copolymers, these random copolymers have a specific preference for solubilising aromatic over aliphatic oils. Increasing hydrophobicity of the copolymer enhances the solubilisation capacity. SANS has highlighted that aggregates become swollen and more uniform/spherical with increasing concentration of aromatic solubilise, and that the aromatic solubilise partitions throughout the random copolymer aggregates.

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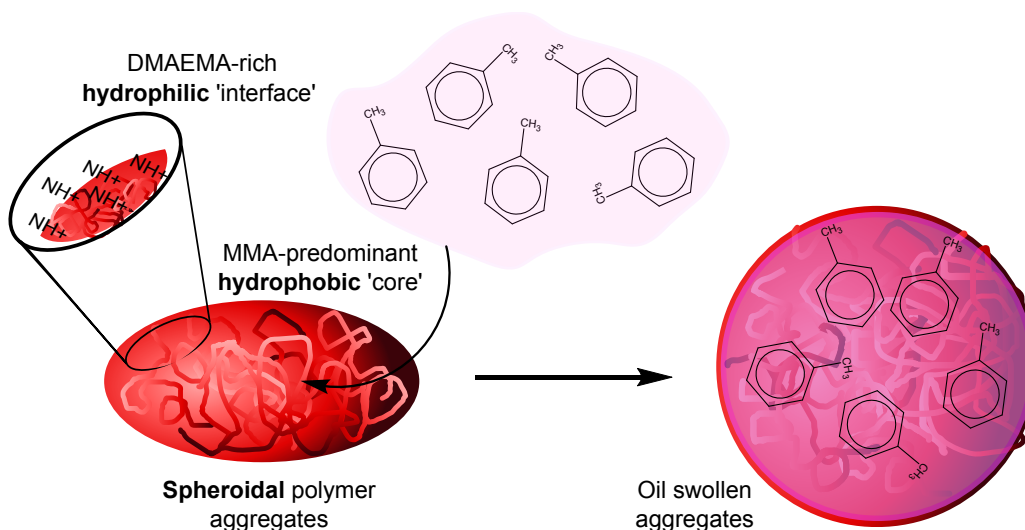
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*Keywords:* Solubilisation, random copolymers and small-angle neutron scattering.

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## Graphical Abstract



## 1. Introduction

It has long been known that surface-active molecules can greatly enhance the aqueous solubility of hydrophobic species, which would otherwise be only sparingly water-soluble. [1, 2] The ancient Egyptians combined vegetable oils with alkaline salts to form soaps over 3000 years ago, probably without understanding the intricacies of micellisation! More recently, with the advent of controlled polymerisation techniques, [3, 4, 5] attention has shifted to block copolymers. Polymer micelles with well-defined hydrophobic/hydrophilic molecular architectures can be effectively loaded with hydrophobic drug compounds, and this has fuelled fervent research in this area. [6, 7]

Another important application of surfactants is for templating mesoporous materials. [8, 9] In particular, Pluronics have found a niche in this area. [9, 10] Pluronics are commercially available block copolymers of poly(ethylene oxide) and poly(propylene oxide). Pluronic P123, for instance, is used to synthesise SBA-15 mesoporous silica. [8] The initial structure of polymer micelles and their modification (by temperature, pH and solubilisation of hydrophobic oils) strongly impact the final mesoporous structure of hybrid materials. [9, 10] Other common applications of Pluronics include detergency, emulsification and fermentation. [11, 12] For this reason,

there is an abundance of literature dealing with solubilisation by Pluronics. [13, 14, 15, 16, 17, 18] Most notably, small-angle neutron scattering (SANS) has been applied to charactering Pluronics in the presence of hydrophobic oils. [10, 13, 14, 18] SANS is a particularly powerful characterisation tool for multi-component systems, given that deuterated chemicals are readily available. [19] By selectively deuterating different parts of a multi-component system, the polymer and solubilised domains can be discriminated, allowing a wealth of detailed structural information to be extracted from subsequent data analyses.

Although, block copolymers exhibit predictable and controllable self-assembly properties (owing to their structural regularity and compositional tuneability) they remain challenging and expensive to synthesise in pure forms. [20, 21] On the other hand, random copolymers are prepared in comparably straightforward synthesis, usually in a one-step co-polymerisation. [22] Even so, studies of random copolymers capable of solubilising hydrophobic oils are seldom reported. This is primarily a result of the inherent challenges of directing the self-assembly of random copolymers into suitable aggregated structures in water. Studies that have been reported almost exclusively focus on enhancing the solubility of hydrophobic drugs. [23, 24] Olea and coworkers did report the partitioning of substituted phenols between water and ‘intramolecular micelles’ formed from potassium salts of poly(maleic acid-*co*-1-olefins). [25] From measuring the distribution coefficients, the Authors speculated that these single chain polymer aggregates could solubilise phenols better than sodium dodecylsulfate surfactant, but less well than block copolymer micelles.

Recently, the synthesis and properties of a heterogeneous copolymer (which can be loosely termed as blocky or ‘lumpy’) has been reported (see ref. and Supporting Information.) [26] This copolymer, poly(methyl methacrylate-*co*-2-dimethylaminoethyl methacrylate) (PMMA-*co*-PDMAEMA), forms intermolecular aggregates when the mol % DMAEMA is low, so that hydrophilic-rich DMAEMA chains stabilise a MMA predominant core, in mildly acidic conditons (pH  $\sim$  4, so DMAEMA is positively charged). In this study the ability of these types of aggregates to solubilise hydrophobic oils (both aliphatic and aromatic) is assessed and where possible compared with common surfactants from the literature. SANS (where the contrast is systematically varied) has been exploited to monitor the morphology of the aggregates with respect to solubilising oils. Proving an example of a random copolymer capable of effectively solubilising certain hydrophobic oils is an important step for developing industrially relevant and commercially viable copolymer systems.

## 2. Materials and Methods

### Materials

Pluronic P123 is a tri-block poloxamer, with the nominal chemical formula Poly(ethylene glycol)<sub>20</sub>-*block*-poly(propylene glycol)<sub>70</sub>-*block*-poly(ethylene glycol)<sub>20</sub>. The P123 used in this study has a number-average molecular weight,  $M_n \sim 5.8 \text{ kg mol}^{-1}$  and was supplied by Sigma-Aldrich (UK). Low molecular weight surfactants, sodium dodecylsulfate (SDS,  $\geq 99 \%$ ) and **hexadecyltrimethylammonium bromide** (CTAB, 99 %) were supplied by Sigma-Aldrich (UK) and Alfa Chemicals (UK) respectively. Hydrophobic dye, Orange OT (also known as Solvent Orange 2 or 1-(o-Tolylazo)-2-naphthol) and hydrophobic solvents: toluene ( $\geq 99 \%$ ) 1,3,5-trimethylbenzene (mesitylene, 98 %) and heptane ( $\geq 99 \%$ ) were all supplied by Sigma-Aldrich (UK). Toluene-d<sub>8</sub> (99 atom % D) and deuterium Oxide (99 atom % D) were also supplied by Sigma-Aldrich (UK).

### Synthesis and characterisation of copolymers

A series of random copolymers of (PMMA-*co*-PDMAEMA) with different mol fraction of DMAEMA were prepared by aqueous emulsion polymerisation. The synthesis and self-assembly in aqueous solution of this copolymer system has been reported previously[26] **and is treated briefly in the Supporting Information.** Table 1 gives the properties of synthesised copolymers (and concomitant aqueous aggregates) used in this study.

### Solubilisation capacity experiments

**In this study, the solubilisation capacity  $S_{dye}$  is defined as the concentration of solubilised dye per  $\text{mg mL}^{-1}$  of surfactant.**  $S_{dye}$  was assessed for low-molecular weight surfactants and polymeric surfactants by UV-visible spectroscopy, using a Thermo Evolution-300 spectrometer. Surfactant-dye

Table 1: Properties of synthesised copolymers used in this study. <sup>a</sup> Mol % of DMAEMA, by <sup>1</sup>H NMR. <sup>b</sup> Weight-average molecular weight (dispersity,  $\bar{D} = M_w/M_n$  is given in parenthesis), by gel-permeation chromatography (GPC). <sup>c</sup> Hydrodynamic diameter of aggregates in water at pH 4.2, by dynamic-light scattering (DLS).

<i>Code</i>	<i>DMAEMA content</i> <sup>a</sup> /mol%	$M_w(\bar{D})$ <sup>b</sup> /( $\text{kg mol}^{-1}$ )	$D_h^c$ /nm
<i>CP</i> – 1	4.9	15.8 (1.9)	27.4
<i>CP</i> – 2	6.3	15.3 (1.9)	30.1
<i>CP</i> – 3	7.8	14.2 (1.8)	25.6

solutions were measured in fused quartz cuvettes with path length of 1 cm. Quantitative assessment of the concentration of solubilised dye was attained  
 90 by applying the Beer–Lambert law,  $A = \epsilon bc$ , where  $A$  is absorbance,  $\epsilon$  is the molar extinction coefficient of the chromophore,  $b$  is the optical path-length and  $c$  is the chromophore concentration. The absorbance maximum of the lowest  $\pi$ – $\pi$  energy transition of the hydrophobic dye, Orange OT, was observed at  $\lambda_{max} = 488$  nm in hexane,  $\lambda_{max} = 492$  nm in 2-propanol,  
 95 at  $\lambda_{max} = 494$  nm in methyl methacrylate and at  $\lambda_{max} = 498$  nm in water. Concentration of solubilised dye was calculated from the absorbance  $A$ , using the molar extinction coefficient  $\epsilon$  of the dye in 2-propanol =  $1.34 \times 10^4$  L cm<sup>−1</sup> mol<sup>−1</sup>.

To determine  $S_{dye}$  of OT dye by the surfactants, an excess of dye (sufficient to ensure saturation) was added to the surfactant solutions present at  
 100 concentrations comfortably above the respective critical micelle (or association) concentration. Saturated dye samples were then stirred for 5 days at 20 °C to ensure equilibration. Following this, samples were allowed to stand for 2 days to permit the unsolubilised dye to settle. Remaining excess dye  
 105 was removed by filtration using a Millipore 0.45  $\mu$ m disposable filter, prior to measurement by UV-visible spectroscopy.

### *Solubilisation of oils*

Hydrophobic oils (aromatic) toluene and 1,3,5-trimethylbenzene as well as (aliphatic) heptane were added to aqueous solutions of the CP copolymers.  
 110 A relatively high concentration of polymer (5 % w/w in water) was chosen, in order that above the solubility capacity a clear separated layer could be observed by eye. Polymer dispersions appear weakly translucent to the eye and this provides sufficient contrast with the upper separated layer, which forms when the concentration of the swelling agent exceeds the solubilising–  
 115 volume capacity,  $S_{oil}$ . In reference to the oils,  $S_{oil} = \phi_{solvent}/\phi_{polymer}$  where  $\phi$  is the volume fraction. CP copolymer dispersions were diluted from an aqueous stock solution (pH 4.2,  $\sim 20$  % w/w). Oil–polymer mixtures were stirred for 5 hr and left to equilibrate for at least 1 day in sealed vials before characterisation. Experiments were carried out three times in parallel and  
 120 the difference in observed  $S_{oil}$  was found to be no more than 0.05 across all oil–polymer mixtures.

### *Characterisation of copolymer aggregates with oils*

Dynamic light scattering (DLS) measurements were collected at 25 °C on a Malvern Nano ZS (4 mW HeNe laser, 633 nm  $\lambda$ ). DLS measurements were  
 125 performed in triplicate on highly dilute aqueous dispersions (10 mM solution of KNO<sub>3</sub> in deionized water). Prior to measurements, samples were filtered

(Whatman, 0.45  $\mu\text{m}$  pore size) to remove dust and particulates. The particle size distribution as described in the text is given by the polydispersity index,  $\text{PDI} = [(\text{width of particle size distribution}/\text{mean particle size})^2]$ . **Reported**  
 130 **uncertainties are the standard deviations of all data collected, from a minimum of three replicates.**

SANS measurements were performed on the Sans2D instrument at ISIS Pulsed Neutron Source (Didcot, UK). A simultaneous Q-range of 0.004-0.7  $\text{\AA}^{-1}$  was achieved using an instrument set-up with the source-sample and sample-detector distance of  $L_1=L_2=4$  m with the 1 m<sup>2</sup> detector offset vertically at 60 mm and 100 mm sideways. Samples were kept in Hellma fused quartz cells, with path length of 2 mm and measured at 25 °C. **Aqueous**  
 135 **polymer-oil mixtures were diluted in water (of specific neutron scattering length density- see later) so that the polymer particle volume fraction was  $\sim$**   
 140  **$\phi = 0.005$ .** Raw SANS spectra were corrected for scattering from the solvent and cell using the instrument-specific software, Mantid, [27] and set to an absolute intensity scale ( $\text{cm}^{-1}$ ). [28] Data have been fitted, as described in text and in the Supporting Information, using SasView small-angle scattering software. [29]

#### 145 *SANS theory*

In a SANS experiment, the intensity (I) of scattered neutrons is measured as a function of momentum transfer (or wave-vector, Q.)  $Q = (4\pi/\lambda)\sin\theta$ , where  $\lambda$  is the neutron wave length and  $2\theta$  is the scattering angle. The normalised intensity per unit volume V of N homogeneous isotropic scatterers  
 150 of volume  $V_p$  and scattering length density  $\rho_p$ , dispersed in a solvent of scattering length density  $\rho_s$  is

$$I(Q) = \phi V_p (\rho_p - \rho_s)^2 P(Q) S(Q)$$

where  $\phi = (N/V)V_p$  and is the particle volume fraction, the function  $P(Q)$  is the particle form factor **and  $S(Q)$  is the structure factor, which describes the scattering due to inter-particle correlations.**

155 In the high-Q regime, scattering originates from local particle interfaces. Porod's law relates the scattering intensity,  $I(Q)$  with the total interfacial area,  $S$  as  $Q \rightarrow \infty$  for any particle form factor, provided that interfaces are smooth

$$\{I(Q)Q^4\}_{Q \rightarrow \infty} = 2\pi(\rho_p - \rho_s)^2 \left( \frac{A}{V} \right)$$

a plot of  $\{I(Q)Q^4\}$  against Q allows the specific surface area,  **$(A/V)$  to**  
 160 **be approximated from the asymptotic intensity.** An estimate of the particle

radius is also given by the first maximum in the Porod plot,  $r_{porod} \approx 2.7/Q_{max}$ . Although, this relation makes the assumption that particles are monodisperse spheres.

### 3. Results and Discussion

#### 165 3.1. Solubilisation capacity of aqueous solution surfactants

The solubility capacity,  $S_{dye}$  of the random CP copolymers was measured with the hydrophobic dye Orange OT and compared with the performance of reference low molecular weight surfactants and Pluronic triblock P123 polymer. The results of the solubilisation study are reported in Table 2. As with most solubilisation study, drawing definitive conclusions is not always straightforward. The observed  $S_{dye}$  is strongly impacted by the chemical nature of the dye [30] and correlating macromolecule composition/structure with solubilising capacity across different surfactant systems should be treated with caution. [31] Nevertheless, this study provides a useful comparison of the solubilising performance across the CP series and with respect to common surfactants from the literature.

Table 2: Solubilisation of hydrophobic dye, Orange OT by surfactants, as determined by UV-vis spectroscopy.  $S_{dye}$  is the solubilisation capacity of the surfactant, = concentration of solubilised dye normalised to 1 mg mL<sup>-1</sup> of surfactant.  $\lambda_{max}$  is the absorbance wavelength maximum of the dye in either solvent or surfactant aggregate solutions.

<i>System</i>	$\lambda_{max}/nm$	$S_{dye}/mg\ L^{-1}$
<i>CP – 1</i>	496.0	60.8
<i>CP – 2</i>	494.5	68.1
<i>CP – 3</i>	493.5	73.0
<i>P123</i>	495.5	70.6
<i>SDS</i>	491.0	29.2
<i>CTAB</i>	492.0	40.9
<i>water</i>	498.0	2.9
<i>methyl methacrylate</i>	494.0	<i>n/a</i>
<i>2 – propanol</i>	492.0	<i>n/a</i>
<i>hexane</i>	488.0	<i>n/a</i>



Directing attention first to solvatochromatic effects, i.e.  $\lambda_{max}$  of the dye, it can be seen that with increasing polarity of the solvent there is a modest increase in the absorbance maxima,  $\lambda_{max} = 488$  nm in hexane shifting to  $\lambda_{max} = 498$  nm in water (dye is only sparingly soluble in water). Typically,  $\lambda_{max}$  can inform on the loci of solubilisation, i.e. is the dye solubilised predominantly in the micelle cores, in the corona/headgroups of the amphiphiles, or at the interface between the cores and corona. [32, 33] Across the new CP series, as the content of hydrophilic DMAEMA is reduced,  $\lambda_{max}$  is blue shifted. The random ('lumpy' or blocky, but critically not statistically random) microstructure of the copolymers, along with their broad chemical composition distribution ( $\bar{D}$ ) means that the copolymers aggregate in such a way to form hydrophilic DMAEMA-rich regions at the interface of the aggregates (which can loosely be termed the 'corona') stabilising MMA predominant cores. [26] Even so, charged DMAEMA groups are still present in the core (or aggregate interiors). Thus, reducing the mol content of DMAEMA will reduce the net polarity of the aggregates, which seemingly enhances the ability of the aggregates to solubilise hydrophobic dye molecules. Given that an increase in  $S_{dye}$  accompanies a reduction in  $\lambda_{max}$  it could be interpreted that the dye molecules partition throughout the aggregates. If the dye were to show a preference for proximity to the more DMAEMA-rich aggregate interface (corona) then  $\lambda_{max}$  would be expected to be approximately constant with DMAEMA content.

Triblock P123 shows a  $\lambda_{max} = 495.5$  nm, implying that the dye is solubilised in a more polar environment and not in the hydrophobic cores. This is consistent with other solubilisation studies into amphiphilic block copolymers. [31] Interestingly, for the low-molecular weight surfactants  $\lambda_{max}$  was shifted to noticeably lower wavelengths, suggesting that dye molecules were mainly solubilised in the interior of the micellar cores. Also it should be noted that the low-molecular weight surfactants have much smaller polar headgroups than the polymeric surfactants, and the tails should be expected to be more hydrophobic than both the P123, which includes ester moieties in the hydrophobic segments and CP copolymers with random hydrophilic groups interspersed throughout the polymer.

For the CP series increasing hydrophobicity leads to an increase in  $S_{dye}$ . CP-1, the most hydrophobic of the copolymers, increased the solubility of the dye in aqueous solution by 25 times compared with pure water. Even the more hydrophilic CP-3 could solubilise the hydrophobic dye more effectively than both low molecular weight surfactants. Of the low molecular weight surfactants CTAB out-performed SDS and this could be either due to the longer tails of CTAB ( $C_{16}$  versus  $C_{12}$  for SDS) and/or the dye could have a greater affinity for the trimethylammonium headgroup over the the sulfate

headgroup of SDS. Further, the CP series performed at least comparably with P123. It is not unreasonable to assume that the CP series random copolymers could possess a solubilising capacity comparable to other amphiphilic diblock copolymers, with the caveat that the composition/chemical nature of copolymers and chemical structure of the dye inevitably makes comparisons by this method indirect.

### 3.2. Solubilisation of oils by CP random copolymers

Figure 1 presents the solubilisation volume capacity  $S_{oil}$  of CP copolymers with hydrophobic oils, toluene, 1,3,5-trimethylbenzene and heptane. Solubilisation-volume capacity is expressed here as a volume ratio of the polymer and the oil, such that  $S_{oil} = \phi_{oil}/\phi_{polymer}$  where  $\phi$  is the respective volume fraction. From first inspection, it is evident that across the CP series there is a specific solubilising preference for (aromatics) toluene and 1,3,5-trimethylbenzene over (aliphatic) heptane. In fact, CP-2 was found to be able to solubilise almost 5 times the volume of toluene ( $S_{oil} = 1.45 \pm 0.05$ ) compared with heptane ( $S_{oil} = 0.30 \pm 0.05$ ). There is a small preference for solubilising toluene over 1,3,5-trimethylbenzene. The solubility in pure water for all the hydrophobic compounds is very low (toluene =  $0.52 \text{ g L}^{-1}$ , 1,3,5-trimethylbenzene =  $0.05 \text{ g L}^{-1}$  and heptane =  $0.003 \text{ g L}^{-1}$  at  $25^\circ\text{C}$ .) A comparison of the respective water solubilities of the hydrophobes perhaps represents a logical place to start. Exclusively based on the very low water solubility of heptane it might be expected to be a poor solvent for the CP copolymers, which contain some interior polar groups. Also it is conceivable that the cationic quaternary ammonium groups of DMAEMA may interact with the aromaticity of toluene and 1,3,5-trimethylbenzene.

A more full appreciation of this specific solubilisation behaviour can be attained with reference to the thermodynamic theory for the solubilisation of classic surfactant and block copolymer systems. [34, 35] For conventional low-molecular weight surfactants the amount (number of moles) that can be solubilised decreases with increasing molecular volume of solubilisate. In other words the volume available for the solubilisate in micellar domains is essentially fixed. The reason being, is that the equilibrium surface area occupied by micelles per surfactant is governed by interactions at the water-micelle interface. [35] However, molecular volume cannot account for the difference in solubility observed between say heptane and 1,3,5-trimethylbenzene, which have comparable molecular volumes. This can be resolved by recognising the lower interfacial tension (solvent-water) of aromatic versus aliphatic oils, remembering that interactions at the water-micelle interface determine micellar volumes. Introducing the so called volume-polarity parameter ( $\sigma_s v_s^{2/3}/kT$ ),

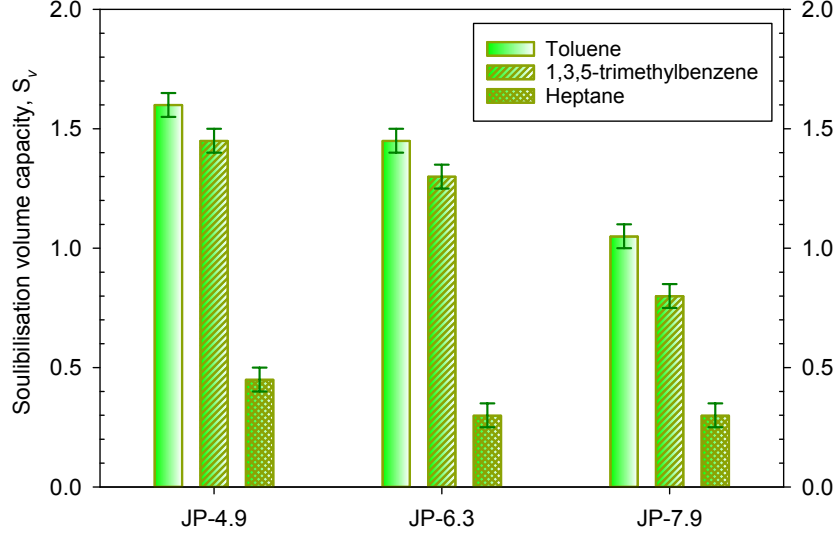


Figure 1: Solubilisation volume capacity  $S_{oil}$  of CP polymers with hydrophobic oils: toluene, 1,3,5-trimethylbenzene and heptane.  $S_{oil} = \phi_{oil}/\phi_{polymer}$  where  $\phi$  is the respective volume fraction. From CP-1 to CP-3 the mol content of DMAEMA increases (i.e. the hydrophilicity of copolymers is increased.)

where  $\sigma_s$  is the solubilisate–water interfacial tension,  $v_s$  is the molecular volume of the solubilisate and  $kT$  is the thermal energy, was able to adequately describe the molar solubilisation capacity of many common low molecular weight surfactants. [36]

However, it was found that this parameter could not satisfactorily scale the solubilisation capacity of block copolymers with different solubilisates. [34] In this case the solubility capacity varied to a much greater degree and so is more akin to the results observed for the CP copolymers in this study. Of course there are important differences in the manner in which (block) copolymers and low molecular weight surfactants self-assemble. [37] Being comprised of many monomers, polymers tend to occupy a larger area at the interface, in order to maximise configurational degrees of freedom of the chains in the inner-aggregate core. Conversely, low-molecular weight surfactants have comparably short chains (and occupy less configurations) and so take up a much smaller area, so as to minimise the free-energy of the interface. For this reason, interactions in the cores rather than at the interfaces are thought to be more important in terms of solubilisation for (block) copolymers. [35] So, it follows that the Flory–Huggins interaction parameter,  $\chi_{sp}$  could help to to correlate experimental data with some theoretical

considerations. In this context  $\chi_{sp}$  is calculated using Hildebrand solubility parameters, as follows

$$\chi_{sp} = (\delta_s - \delta_p)^2 v_s / kT$$

where  $\delta_s$  is the solubility parameter of the solubilisate and  $\delta_p$  is the solubility parameter of the polymer which forms the cores of the polymer micelles. As the magnitude of  $\chi_{sp}$  decreases, the solubilisation capacity should be expected to increase. For a small value of  $\chi_{sp}$  (i.e  $\chi_{sp \rightarrow 0}$ ) the small positive enthalpic effect can be overcome by the entropic effect, thus enhancing the solubilisation capacity. Table 3 provides some selected solubility parameters. It is evident that an increase in  $|\delta_s - \delta_p|$  will be accompanied by an increase in  $\chi_{sp}$  and therefore a reduced solubilisation capacity. For instance in the P123 tri-block for the non-polar poly(propylene oxide) (PPO) block (where most of the solubilisate is expected to locate)  $\chi_{sp} = 0.028$ . Whilst for the polar poly(ethylene oxide) PEO block  $\chi_{sp} = 0.45$ , when the solubilisate is toluene. Replacing the solubilisate for heptane now means that for the PPO block  $\chi_{sp} = 0.894$  and for the PEO block  $\chi_{sp} = 2.24$ .

Returning to the CP system, it is important to keep in mind that the

Table 3: Selected Hildebrand solubility parameters at 25 °C. [38]

<i>Polymer or surfactant tail</i>	<i>solubility parameter (<math>\delta_p</math>)/(J cm<sup>-3</sup>)<sup>1/2</sup></i>
<i>PMMA</i>	19.3
<i>PEO</i>	20.5
<i>PPO</i>	18.5
<i>PNIPAM</i>	23.5
<i>C<sub>12</sub> – tail</i>	15.9
<i>C<sub>16</sub> – tail</i>	16.3
<i>Solubilisate</i>	<i>solubility parameter (<math>\delta_s</math>)/(J cm<sup>-3</sup>)<sup>1/2</sup></i>
<i>heptane</i>	15.1
<i>1, 3, 5 – trimethylbenzene</i>	18.0
<i>toluene</i>	18.2
<i>water</i>	40.8

random nature of the copolymer means the application of the Flory–Huggins interaction parameter should be treated as a gross approximation. Notwithstanding, it is no doubt useful in predicting the performance of the CP aggregates in solubilising different solubilisates. The small difference in solubility parameters for toluene and 1,3,5-trimethylbenzene explains the slight preference for solubilising toluene. As the mol content of DMAEMA is reduced (from CP–3 to CP–1) the ability to solubilise the aromatics is enhanced, for toluene  $S_{oil} = 1.05 \pm 0.05$  for CP–3 increasing to  $1.60 \pm 0.05$  for CP–1 (Figure 1). A similar enhancement of  $S_{oil}$  for 1,3,5-trimethylbenzene is also observed. Across the CP series (from CP–3 to CP–1) the relative magnitude of  $\delta_p$  should be expected to fall, since there will be less polar DMAEMA in the aggregate interior.

Interestingly, this means that from widely available tables of  $\delta_s$  the solubilisation capacity for a respective solubilisate could be estimated. Given that there is an inherent preference for specific solubilisates according to  $\delta_p$  (the polarity of the core or aggregate interior) these type of aggregates represent a promising system for applications concerned with specific solubilisation, for example for water or soil remediation [12, 39] (for which certain phenolic and polycyclic hydrocarbons, for instance are a major health concern). CP copolymers could be made to solubilise significant volumes of aromatics by increasing the copolymer concentration. At 15 % v/v CP–1 could theoretically solubilise up to 0.24 mL of toluene per mL of aqueous polymer dispersion. Further, the polarity of the aggregate interior can be broadly tuned by adjusting the monomer feed ratio (or combination) in a simple emulsion polymerisation (compared with the more challenging synthesis of block copolymers). Currently however, using the recently published synthetic route to self-assembled CP aggregates (in aqueous solution) have only been reproducibly prepared in quite a narrow compositional range.

### 3.3. Copolymer aggregates with oils—characterisation by DLS

Dynamic-light scattering (DLS) was used to monitor any changes in hydrodynamic size of the CP-aggregates with solubilisation of oils. In the discussion that follows, to facilitate comparisons between systems, the solubilisation is described in terms of the fraction,  $f$  of the maximum  $S_{oil}$  (i.e.  $S_{oil\ max}$ ) for the respective oil. So that  $f = S_{oil}/S_{oil\ max}$ . Figure 2 gives the particle size distribution of CP–2, as a function of  $f$  for toluene. Perhaps somewhat surprisingly, the hydrodynamic  $Z$ -average diameter ( $D_h$ ) of the CP–2 aggregates appears to decrease slightly with increasing  $f$ . (When  $f = 0.00$   $D_h = 30.1 \pm 0.3$  nm, when  $f = 0.95$   $D_h = 27.2 \pm 0.4$  nm.) This would tend to suggest that aggregates are not physically swelling to accommodate increasing volumes of the solubilisates, as  $f$  approaches 1. It is also apparent

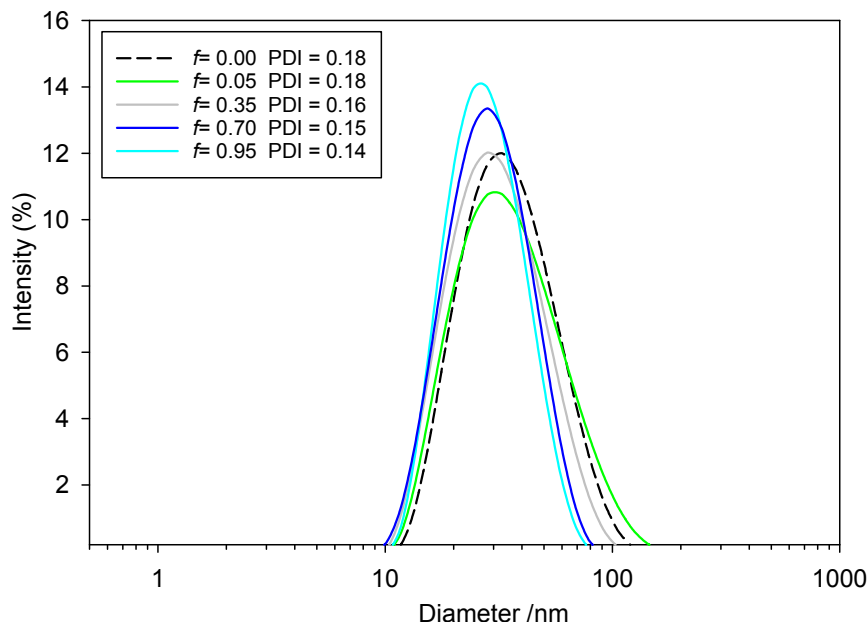


Figure 2: Intensity-weighted hydrodynamic size distribution for CP-2 as a function of the fraction of maximum solubilisation  $f$  of toluene. The PDI at respective  $f$  values is given in the legend. As  $f$  is increased the PDI reduces, suggesting aggregates are becoming more uniform and potentially may be becoming more spherical.

from Figure 2 that the polydispersity index (PDI, see Materials and Methods) shifts to lower values, as  $f$  increases. (When  $f = 0.00$  PDI = 0.18, when  $f = 0.95$  PDI = 0.14.) This implies aggregates may be becoming more uniform as they solubilise greater volumes of toluene. The full DLS data set for all oils, across the CP series, is provided in the Supporting Information. The slight reduction in  $D_h$  and accompanying decrease in PDI is observed universally across the CP series for both (aromatics) toluene and 1,3,5-trimethylbenzene. In the case of heptane there is negligible change in the hydrodynamic size properties, as measured by DLS. This can be attributed to the small volumes of heptane, which can be effectively solubilised by the CP aggregates.

In DLS the hydrodynamic size is represented by a single value, i.e the apparent diameter of a sphere that has the same translational diffusion coefficient as the measured particle. DLS measurements are heavily-weighted at larger particle sizes (intensity of scattered light  $\propto r^6$ .) DLS data collected in this study, implies that CP aggregates are becoming more uniform (less polydisperse) as  $f$  increases, which may be concomitant with a small reported reduction in the  $Z$ -average diameter, as oppose to a physical shrinking of the

aggregates. Whether or not the shrinking of aggregates is a measurement artefact or a real physical behaviour can be substantiated by small-angle neutron scattering (SANS) measurements, which are described in the following section.

### 3.4. Copolymer aggregates with oils—characterisation by SANS

SANS is sensitive to the internal structure of particles. [19] Assuming the scatterers are sufficiently dilute (and strong inter-particle interactions are screened,) the shape of the scattering profile is a consequence of the size, shape and polydispersity of particles, as well as the contrast between the scatterers with respect to the solvent. The latter makes SANS a particularly powerful characterising tool for multi-component systems, given that deuterated chemicals can be obtained. By selective deuteration, the scattering profile can result solely from either the copolymer aggregates or the oils, and this can be compared to the scattering from the ensemble particles.

From a previous study, the morphology of the oil-free CP type aggregates was found to be consistent with an oblate-spheroid form factor, i.e. the particle shape is described by an equatorial axis,  $r_b$  and a polar axis,  $r_a$ , where  $r_b > r_a$ , so as to resemble a flattened sphere. [26] It is not necessarily straightforward to accurately describe the scattering which originates from spheroidal shapes. In this case, applying sensible constraints (from DLS data and parameters known from the sample preparation, i.e.  $\phi$ ,  $\rho_p$  and  $\rho_s$ ) polymer aggregates are best fit to oblate ellipsoids, as oppose to prolate ellipsoids or polydisperse spheres. Notably, from this same study, the SANS profiles of the CP-aggregates were absent of high-Q scattering features, indicative of well-defined core-shell form factors. This could be ascribed to the thin, solvent swollen corona (probably  $\sim 0.3$  nm) and closely analogous chemical structures of PMMA and DMAEMA, meaning there should be minimal neutron contrast between a DMAEMA-rich corona and MMA-poor aggregate interior. Fitting the data to simple shape form factors, compared with more complex core-shell models should vastly simplify the data interpretation, reducing the number of fit parameters and so improving the confidence of the data fitting.

SANS measurements were performed on the CP-2 system with toluene as the added oil. Measurements on this system are thought to be representative of the wider behaviour of the CP random copolymers with aromatic oils, as is suggested by DLS data. CP-2 was measured at three different solvent-component contrasts (where the component responsible for the scattering is given in bold below), using the following notation: hydrogenated = H, deuterated = D and contrast-matched = cm:

- ‘ensemble’ = H-CP-2/H-toluene/D-water
- ‘oil’ = H-CP-2/D-toluene/water cm-to-CP-2
- 390 • ‘polymer’ = H-CP-2/D-toluene/water cm-to-D-toluene

Figure 3 presents the scattering profiles (and solid lines are model fits) at the three different contrasts. For the ‘ensemble’ and ‘polymer’ contrasts, inclusion of an effective structure factor marginally improved the fitting of the data at low-Q. In mildly acidic conditions (for aqueous polymer-oil mixtures pH  $\sim$  4.5) DMAEMA is charged, and so inter-particle interference effects arise due to screened electrostatic repulsion between the charged polymeric aggregates, even at quite dilute polymer volume fraction ( $\phi \sim 0.005$ .) Model fit parameters are tabulated in Table 4. Details of the model fits and the scattering-length densities of components are given in the Supporting Information. Three main conclusions can be drawn from the data:

Table 4: Model fit parameters for CP-2 aggregates with toluene. The ‘oblate’ model refers to an oblate ellipsoid fit, where equatorial axis,  $r_b >$  the polar axis,  $r_a$ .  $r_{porod}$  is the approximate radius estimated from Porod plots.

<i>Contrast</i>	<i>f</i>	<i>model</i>	$r_a/nm$	$r_b/nm$	$r_b/r_a$	$r_{porod}/nm$
<b>ensemble</b>	0.00	oblate	4.35	11.98	2.8	7.5
<b>ensemble</b>	0.33	oblate	4.36	12.58	2.9	6.9
<b>ensemble</b>	0.66	oblate	6.19	12.67	2.1	8.8
<b>ensemble</b>	0.95	sphere	9.53	9.53	$r_b = r_a$	10.3
<b>oil</b>	0.33	oblate	4.09	12.68	3.1	7.1
<b>oil</b>	0.66	oblate	6.13	12.95	2.1	8.8
<b>oil</b>	0.95	sphere	9.43	9.43	$r_b = r_a$	10.3
<b>polymer</b>	0.33	oblate	4.46	12.75	2.9	6.7
<b>polymer</b>	0.66	oblate	6.10	12.97	2.2	8.8
<b>polymer</b>	0.95	sphere	9.61	9.61	$r_b = r_a$	10.2



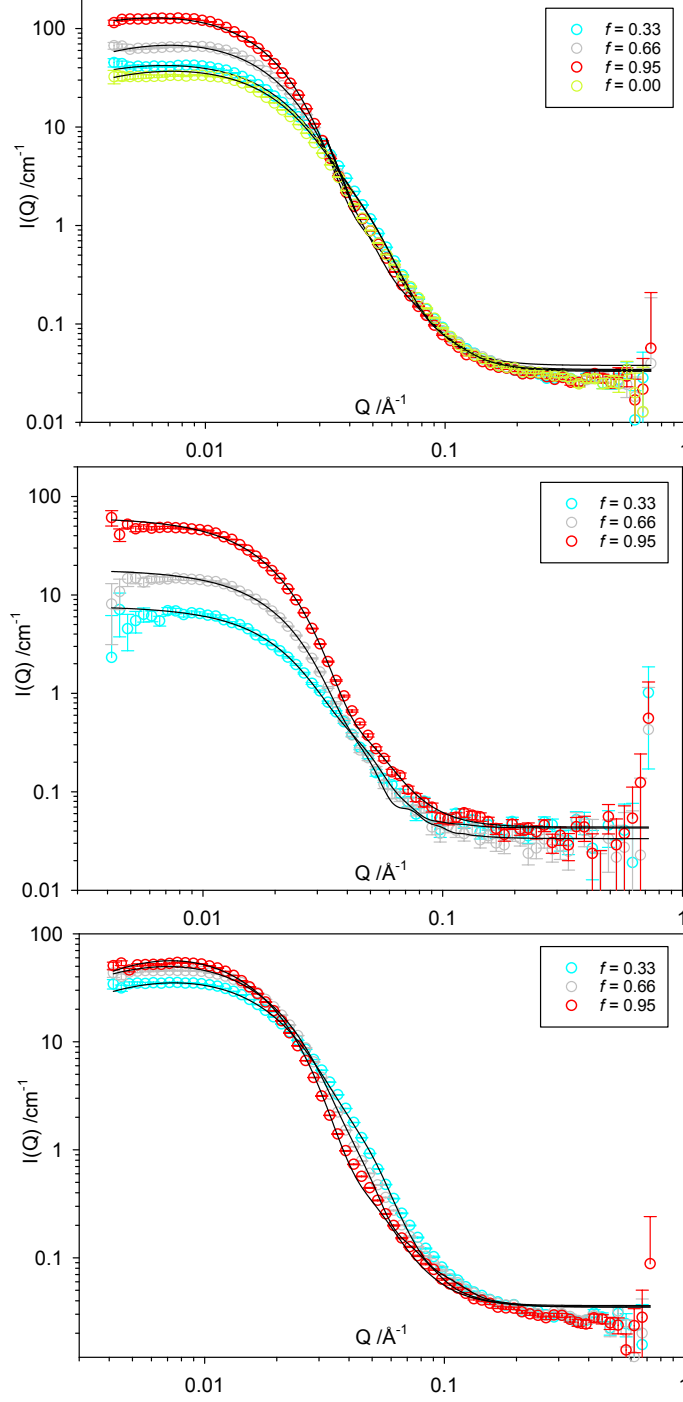


Figure 3: SANS profiles for CP-2 aggregates with toluene as solubiliser.  $f$  is the fraction of maximum solubilisation. Top profiles = **ensemble** contrast. Middle profiles = **oil** contrast. Bottom profiles = **polymer** contrast. Solid lines are model fits.

(1) Contrary to DLS data, SANS implies that aggregates do, in fact, swell with increasing concentration ( $f$ ) of toluene. This is most clearly illustrated by the shifting peak positions of Porod plots (Figure 4.) Indeed, across all contrasts the approximate  $r_{porod}$  increases with  $f$  (final column, Table 4.)  
 405 Porod’s law relates the specific surface area  $(A/V)$  to  $I(Q).Q^4$  as  $Q \rightarrow \infty$ . Assuming that the the number of scattering particles  $N$  is fixed, then  $(A/V)$  should be expected to scale with the particle radius squared. From the approximated  $r_{porod}$ ,  $(A/V)$  ought to increase by a factor of  $\sim 2$ , as  $f$  increases from 0.33 to 0.95, supposing that aggregates were physically swelling. Comparing the values for  $(A/V)$  when  $f$  is  $0.33 = 7.9 \times 10^4 \text{ cm}^{-1}$  and when  $f$   
 410 is  $0.95 = 1.7 \times 10^5 \text{ cm}^{-1}$ ; these values are reasonably close to scaling by a factor of 2. It is important to concede that the approximation of  $r_{porod}$  from the maximum peak position, is only strictly valid for monodisperse spheres. Notwithstanding, an increase in  $(A/V)$  can only mean that aggregates are  
 415 physically swelling to solubilise increasing volumes of toluene.

Interestingly, the degree of swelling observed for CP-2 ( $\sim 14\text{-}20 \text{ nm}$ , by SANS) is comparable to reports of the swelling of Pluronics, despite the quite different chemistries and self-assembly of the macromolecules. Manet et al., reported that the overall size of Pluronic P123 micelles increased from  $\sim 18\text{-}$   
 420  $25 \text{ nm}$  with increasing concentration of toluene, which the Authors termed a ‘hydrophobic swelling agent.’ [10] Lettow and coworkers observed a similar increase in the size of Pluronic micelles, this time with 1,3,5-trimethylbenzene and 1,2-dichlorobenzene. [13]

(2) In accordance with DLS data, aggregates seem to become more uniform as  $f$  increases. When no toluene is present CP-2 aggregates are best fit  
 425 to an oblate spheroid form factor. This is consistent with a previous study. [26] At low toluene content,  $f = 0.33$ , the form factor (and fit parameters) do not unduly change. When  $f$  is increased to 0.66,  $r_a$  increases whilst  $r_b$  remains essentially constant, having the effect of reducing the aspect ratio of the aggregates. At this point, the aggregates can almost be adequately  
 430 described by a (polydisperse) sphere model. However, a better fit (within sensible constraints) is still maintained for an oblate spheroidal form factor. At high  $f = 0.95$  the aggregates are now best described by a (polydisperse) sphere model.

(3) Fit parameters (and models used to fit the data) across all three contrasts are very similar. This means that domains of toluene (from scattering of oil contrast) have essentially the same form factor as the scattering from the polymer and the ensemble (summation) scattering. The absolute intensity is shifted across the different contrasts according to the effective  
 440 particle volume fraction. The upshot being, that toluene seemingly partitions throughout the aggregates, as was tentatively suggested from UV-visible

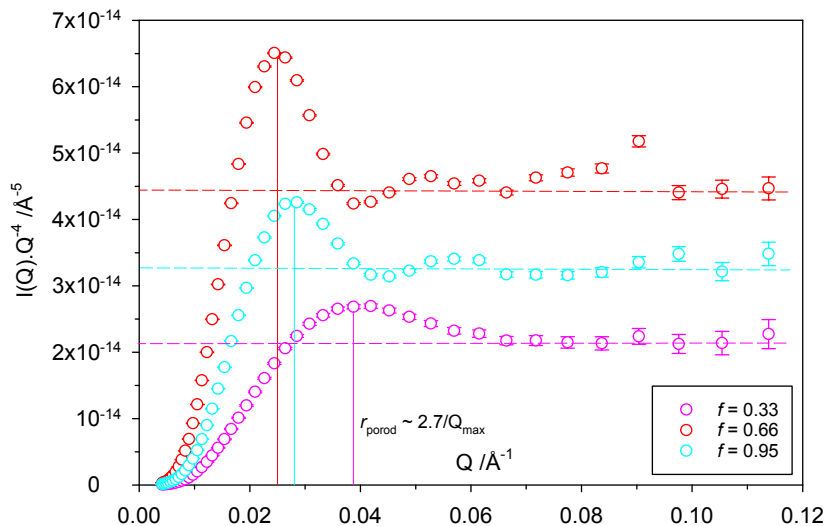


Figure 4: Porod plots (from **polymer** contrast) for CP-2 aggregates with toluene as solubiliser.  $f$  is the fraction of maximum solubilisation. The solid vertical lines give the maximum peak position and in turn the effective Porod radius,  $r_{porod}$ . The dashed horizontal lines give the Porod asymptotes (i.e.  $\{I(Q)Q^4\}_{Q \rightarrow \infty}$ ) which allow estimations of the specific surface areas,  $(A/V)$  to be determined.

spectroscopy. This is probably to be expected given the very thin ‘corona’ which is probably rich in solvent and so ‘invisible’ by SANS. In any case, it is probably unfavourable for toluene to be solubilised in close proximity to the aggregate interfaces.

#### 4. Conclusions

A substantial body of literature now exists for the solubilisation of oils by block copolymers, particularly for Pluronics. [13, 14, 15, 16, 17, 18, 35] Part of this interest stems from a desire to control the structure of block copolymer aggregates for templating mesoporous materials. [9, 10] Studies into solubilisation of oils by random copolymers are quite rare. This is mainly due to the difficulties of directing the self-assembly of random copolymers into suitable nano-structures in aqueous phases. [22] This study reports how a random copolymers, namely poly(methyl methacrylate-*co*-2-dimethylaminoethyl methacrylate) (PMMA-*co*-PDMAEMA) are capable of effectively solubilising aromatic oils, in aqueous systems (at pH 4). After an extensive search of the literature, it appears that this is the first study to report the solubilisation of aliphatic and aromatic hydrophobic oils (as well as characterising changes in the aggregate morphology) by random copolymers.

460 The random copolymers showed a preference for solubilising aromatic oils  
(toluene and 1,2,3-trimethylbenzene) over aliphatic oils (heptane), and this  
is similar to block copolymers. [34] Reducing the mol fraction of (the more  
hydrophilic) DMAEMA across a narrow range (8-5 mol %) improved the  
solubilising performance of the copolymer aggregates. At a high copolymer  
465 concentration (approaching 20 % w/w in water), aggregates could disperse  
significant volumes of aromatic oils, which could have applications in wa-  
ter/soil remediation or other specific solubilisation applications. Small-angle  
neutron scattering (SANS) together with dynamic-light scattering (DLS) re-  
vealed that increasing the concentration of the aromatic solubilisate (toluene)  
470 has the effect of making the copolymer aggregates more uniform and spheri-  
cal.

Recent literature has largely focused on developing ever more complex  
and well-defined macromolecules. [5, 20, 40] This study points in the oppo-  
site direction, and represents an interesting example of how, under the right  
475 conditions, a relatively primitive macromolecule has the potential to perform  
comparably to more well-defined (and more synthetically challenging) block  
copolymers. Designing simpler macromolecules which can fulfil practical in-  
dustrial needs is crucial for preparing commercially viable systems.

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